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PROGRESS

REPORT

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On EXPERIMENTAL AND THEORETICAL INVESTIGATION OF THE RHEOLOGICAL PROPERTIES OF MATERIALS

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RHEOLOGICAL PROPERTIES OF MATERIALS

OBJECTIVE

The further development and testing of the kinetic interpretation of non-Newtonian flow is the primary goal of this work. The development aspects involve the extension of the theory to include interpretation of normal stress data and to allow prediction of viscoelastic characteristics from the kinetic equation and equations of the system. Further experimental testing is now in progress in order to obtain what we feel will be data needed for the confirmation of the time-dependent (thixotropic) aspect of the theory and the proof of the theory's internal consistency. Modifications are in progress to allow data to be obtained to study the normal stress and viscoelastic aspects of the problem.

BACKGROUND

The basic approach and preliminary confirmation of the method has been described in papers by Denny and Brodkey[1] and Denny, Kim, and Brodkey,[2] and in previous progress reports. The theory is based upon the assumption that the nonlinear characteristics can be associated with some structural change of the material, and that reaction kinetics can be applied to this breakdown. The theory allows treatment of time-dependent (thixotropic) materials and their solutions. Two rather complete reviews, in the form of Ph.D. theses, are also now available.[3,4]

PROGRESS AND RESULTS

Our main effort during the last year has been concentrated on obtaining the necessary data to test the theory. This effort involved obtaining a comprehensive set of rate and equilibrium data on pure polymethylmethacrylate and solutions of the pure material. All of this work is now completed and has been reported in the theses by Denny[3] and by Kim.[4] Parts of these theses are being prepared for publication in the technical literature and presentation at scientific meetings. The rate (time-dependent) data proved to be most difficult to obtain in the proper form; nevertheless, enough has been obtained to justify the theory[3] although more and better data are needed for the complete confirmation and proof of the theory's internal consistency. It is this aspect of the problem that most of our current attention is directed. We are trying to establish why the data was difficult to obtain, how we can obtain exactly that which we need, and of course its interpretation.[5] The equilibrium data was much easier to obtain, although a capillary shear system for high shear rate data had to be constructed.[4] In the following paragraphs details of these two works and more recent efforts will be treated. The current problems will be considered in the next section on PLANS.

The time-dependent constant shear data obtained so far has allowed independent evaluation of the several parameters of the theory. In review, the total basic kinetic equation is

$$- dF/dt = k_1 \tau^{p_1} F^m - k_2 \tau^{p_2} (1-F)^n \tag{1}$$

where F, the fraction unconverted, is given by

$$F = \left(\mu^{1/a} - \mu_\infty^{1/a}\right) \Big/ \left(\mu_0^{1/a} - \mu_\infty^{1/a}\right) \tag{2}$$

in which "a" has the assumed empirical value of 3.4. As described in some detail in reference 2, this equation can be evaluated by various standard homogeneous kinetic approaches using rate data. At equilibrium the equation reduces to

$$(1 - F)^n / F^m = K\tau^p \tag{3}$$

where $K = k_1/k_2$ and $p = p_1 - p_2$. A program is available for the evaluation of the constants from steady state data. Table I reviews the three best estimates of which m = 1 and n = 2 was the best. The corresponding values of K and p are given.

TABLE I

$\mu_0 = 5.82 \times 10^6$ poise (350°C)

m	n	K	p
1	2	5.5×10^{-16}	2.37
1	3	4.92×10^{-23}	3.44
2	3	3.38×10^{-24}	3.67

For short periods of time, the basic equation can be integrated for constant shear rate to give

$$\frac{F^{-3.45p_1 - m + 1} - 1}{3.45p_1 + m - 1} = k_1 (\mu_0 s)^{p_1} t \tag{4}$$

which suggests that a plot of log t versus log s (s is shear rate) at constant F can provide an estimate of p_1. k_1 is obtained from the initial slope of a plot of

$$F^{-3.45p_1 - m + 1} = F^{-10.21} \text{ versus } s^{p_1}t = s^{2.96}t$$

Here the value of m must be known to evaluate k_1 but was not needed to obtain p_1. Because of the results obtained in Table I, the vaule of m was taken as unity without further confirmation.

To this point equation (1) is

$$- dF/dt = 1.10 \times 10^{-20}\tau^{2.96}F - k_2 \tau^{p_2}(1 - F)^n \tag{5}$$

The constants still to be determined are those associated with the reverse rate. Thus 1 - F must be fairly large, where fortunately, the rate could be obtained by measuring the slope of the time curve during the recrossing of the gap. From reference 2, equation (1) can be rearranged to

$$dF/dt + k_1 \tau^{p_1} F = k_2 \tau^{p_2}(1 - F)^n \tag{6}$$

which suggests that a plot of the left-hand side versus 1 - F can be used to determine that n = 2. With this known, a log-log plot of

$$\frac{dF/dt + k_1 \tau^{p_1} F}{(1 - F)^2} \text{ versus } \tau \tag{7}$$

will give p_2 as the slope and k_2 as the intercept. For each an average was used, which deviated about 2% or so. Table II gives the final comparison of the results of the equilibrium and the time-dependent evaluation.

TABLE II

m = 1		n = 2
	$K = 5.5 \times 10^{-16}$	
	$p = 2.37$	
$k_1 = 1.10 \times 10^{-20}$		$k_2 = 3.10 \times 10^{-5}$
$p_1 = 2.96$		$p_2 = 0.56$
	$K = k_1/k_2 = 3.5 \times 10^{-16}$	(28%)
	$p = p_1 - p_2 = 2.40$	(0.65%)

Although the results are quite satisfactory, it is apparent that they cannot be considered a real proof of the theory. There is too much possibility of error in the evaluation. Consequently, we have proceeded to modify the instrument[5] as suggested in the last progress report. The present measuring system was pushed to its extreme, which allows tests to be made, but not of the accuracy desired. A number of these runs have been complete and although the response time (now about $\frac{1}{2}$ second instead of the desired 0.05 second) is good enough to allow a reasonable evaluation of the theory to be made, we have uncovered an additional complication associated with the viscoelastic nature of the polymethylmethacrylate. Now that the instrument response has been reduced, we have arrived at the material response which acts the same as the instrument response and masks the initial part of the rate curve preventing us from obtaining the desired data on this material.

As will be noted in the plans, we are now looking and hopefully have found a material that is quite time-dependent in its non-Newtonian properties but shows little if any viscoelastic properties. This material is a nonpolymeric dilute colloidal dispersion. With this material and particularly at higher shear rates, we should be able to get the desired rate curves. These experiments are now in progress.[5]

The rate equation (1) can be modified for solutions to give

$$-dCF/dt = k_1\ \tau^{p_1}(CF)^m - k_2\ \tau^{p_2}[C(1-F)]^n \tag{8}$$

At equilibrium or steady state this rduces to an equation, analogous to (3):

$$K\ \tau^p = (1-F)^n C^{n-m}/F^m \tag{9}$$

Again a program is available for the evaluation of p and K for selected values of m and n. Although more data over a wider range of conditions are required for this type of analysis, it does have the advantage of being at steady state and not being affected by the response problem previously cited.

Ten solutions of the polymer in diethylphthalate with concentrations up to 55 per cent were investigated at 40°C. Several were studied at 55°C also. To supplement the main analysis, the available pure melt data of Denny[3] and of Rohm and Haas at five different temperatures were used. The forward and reverse orders (m and n) could be used as 1 and 2, respectively, for both the solution and melt data. Furthermore, the solution data could be satisfactorily treated as having an average p value of 2.0 and an average K of 7.1×10^{-13}. The usefulness of the theory was demonstrated by a back-calculation of the flow curves using these average values. The flow data were reproduced to within the experimental error for those solutions where it was felt that the data were satisfactory, and generally better represented than could be done by other methods, since alternative correlation methods do not take into consideration the variation of concentration and thus are severely limited.

PLANS

We are currently investigating alternative materials so as to eliminate the material time response problem elucidated in the previous section. When this investigation is complete a new set of time response data will be obtained. In conjunction with this several modifications, briefly mentioned in the previous progress report, are under way. A new normal force system is under test. This system is ideal for fast response measurements without motion of the lower plate, however, one difficulty which we are now trying to resolve, is the system's sensitivity to the shock of the magnetic clutch turning on at the beginning of a run. This situation might be remedied by a modified mounting method.

The special transducer system is new to this type of application, and consequently, the manufacture has been most cooperative in loaning the instrument to us. A second modification is a new variable-speed coupling that can be introduced between our motor and gearbox to allow lower rates of shear to be obtained. We have had some trouble getting to a low enough rate of shear so as to observe the lower Newtonian region. This same coupling can be used to provide an oscillatory motion to the plate, although this is not planned for the immediate future. Finally, consideration has been given to modifications that would be necessary to operate the system as a constant torque device. The necessary parts have been located, but no effort to obtain them will be made for now, since we are not as yet positive that constant torque operation is necessary.

When those factors above have been completed, the final confirmation of the kinetic approach can be made.[5] Upon completion, the kinetic constants will be obtained on solutions of polyisobutylene, with the aim to phenomenologically represent normal stress difference data to be obtained by us[6] and by Markowitz.[7] Parallel to this will be the evaluation of viscoelastic characteristics normally obtained on such materials.[8]

Aside from these efforts, a study is still in progress[9] on an independent measurement of the fractional change that occurs at various shear levels. Such measurements would add strong support to the validity of our interpretation of non-Newtonian behavior.

REFERENCES AND NOTES

1. Denny, D., and R. S. Brodkey, J. Appl. Phys., 31, 2269-74 (1962).

2. Paper presented at Society of Rheology Meeting, Pittsburgh, Pa., October 1964, "Kinetic Interpretation of Non-Newtonian Flow," D. Denny, H. T. Kim, and R. S. Brodkey.*

3. Denny, D., Ph.D. thesis in Chemical Engineering, The Ohio State University, Columbus, Ohio 43210 (1966).

4. Kim, H. T., Ph. D. thesis in Chemical Engineering, The Ohio State University, Columbus, Ohio 43210 (1966).

5. Modification and confirmation are a part of Ph.D. thesis work of L. Jones.

6. To be obtained as a part of Ph.D. thesis of L. Jones.

7. Markowitz, H., Trans. Soc. Rheology, 1, 37 (1957); Phys. Fluids, 8, 200 (1965).

8. To be evaluated as a part of Ph.D. thesis of R. Chase.

9. A part of Ph.D. thesis work by H. Bauer.

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